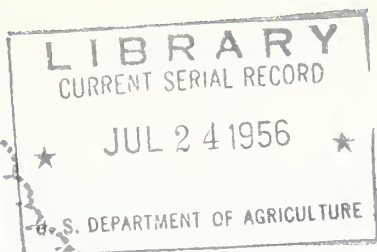


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# A Rapid Method for Determining the Oil Content of Cottonseed



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## SUMMARY

A requisite to sound marketing of a commodity is a standard method for evaluating its quality. Individual lots of cottonseed as sold by farmers vary widely in composition and value indicating the need for a reliable method of grading.

Although cottonseed are purchased from ginneries by oil mills on official grades in most areas of the Cotton Belt, this system of grading is too elaborate, too expensive and time consuming for use on individual lots as sold by farmers.

A method for small lot grading of cottonseed must be simple, rapid and inexpensive. Quality factors of importance are oil content, free fatty acids content of oil, moisture content, protein content, linters content and foreign matter content. The oil content is the most important single factor since it has accounted for from 43 to 60 percent of the value of cottonseed.

Various methods of oil assay that were thought to have promise from the standpoint of application to small lot grading of cottonseed were investigated. These included direct evaporation, precipitation or "salt-ing-out," electrical conductivity, specific gravity, refractive index, heat of combustion, infra-red absorption, dielectric measurement and modified gravimetric methods. All of these except dielectric measurement were found to be impractical or otherwise unsuitable for application to the grading of small lots of cottonseed.

Apparatus based on dielectric measurement has been perfected for the rapid determination of the oil content of samples of cottonseed. The basic elements of this apparatus are a test cell and oil meter for determining the oil content of a sample of cottonseed by the measurement of the dielectric constant of an oil-solvent mixture where the dielectric constant of the solvent is known. Accessory equipment includes: (1) A grinder-extractor of the high speed impact cutter type for the rapid extraction of the oil from the cottonseed sample with the aid of the solvent orthodichlorobenzene, (2) a mechanical air-pressure filter for the filtration of the oil solvent extract and, (3) a bath for controlling the temperature of the oil-solvent mixture in the test cell.

The test cell consists of two concentric metal cylinders, the inner cylinder suspended in and electrically insulated from the outer cylinder and with the space between the two cylinders forming the condenser.

The oil meter is essentially a substitute type radio frequency capacity meter and a cell suitable for measuring liquid dielectrics. The instrument is adjusted to resonance (indicated by a meter) with a fixed condenser in the circuit. The test cell filled with the liquid to be measured is substituted in the circuit for the fixed condenser and a calibrated variable condenser is used to retune the instrument to resonance.

The pressure filtration system consisting of a hand press and air-pressure filter is used to rapidly separate the liquid from the solid ground material. Most of the large lint and hull particles are retained by the hand press, the remainder retained by filter paper in the air-pressure filter. Rapid filtration is aided by the use of a desiccant which removed minute quantities of water in the oil-solvent mixture.

After an examination of more than 100 solvents, orthodichlorobenzene was found most suitable for this application which requires not only a rapid and effective extraction of the oil from cottonseed but also a dielectric constant differing as much as possible from that of cottonseed oil. Other requirements effectively met by this solvent are: a high boiling point to minimize evaporation during sample preparation, non-toxic, non-inflammable, uniformly high purity and relatively low cost.

A series of tests made on cottonseed of greatly varying constituents indicated a correlation of 0.994 with the USDA official chemical method with a standard error of difference of  $\pm 0.15$ .

A determination of the oil content of cottonseed may be completed in ten minutes. Preparation and grinding of the sample is accomplished in seven minutes, filtration and reading the meter in three minutes. Two operators using two grinder-extractors and one meter can make 100 oil determinations in 5.9 man hours. Cost of material is estimated at about \$0.16 per sample.

The official method of analysis requires an estimated 13 man hours for 100 oil determinations with supplies costing an estimated \$0.09 per sample. The overall time required for analysis is 24 hours.

It is concluded that: (1) The principle of dielectric measurement of the oil content of cottonseed is sound and practical. (2) The method is satisfactory from the standpoint of accuracy. (3) The method is sufficiently rapid to make its use practical for measuring the oil content of small lots of cottonseed at gins. (4) The facility with which oil content determinations can be made by means of the dielectric method and the accuracy of the results justify its consideration as an alternate method of oil assay in connection with the official method of grading cottonseed.

It is recommended that: (1) The dielectric meter and cell be redesigned for commercial manufacture. (2) Redesigned units be thoroughly field tested.

## A RAPID METHOD FOR DETERMINING THE OIL CONTENT OF COTTONSEED

by Marion E. Whitten and Charles E. Holaday,  
Cotton Technologists

### IMPORTANCE OF QUALITY ELEMENTS OF COTTONSEED

Within the last 75 years, cottonseed has advanced from a waste product to a major income producer in the Cotton Belt and the products derived from cottonseed are important in the national economy. During the 10 years 1948-53, the farm value of cottonseed averaged over 336 million dollars annually. Therefore, it is important that methods and facilities necessary to equitable and efficient marketing be provided.

A necessary requisite to sound marketing procedures of any commodity is a standard method for evaluating its quality. Since individual lots of cottonseed may differ widely in composition, a reliable method of grading is essential for efficient marketing. The oil content of different lots of cottonseed may vary more than 250 pounds, the meal or cake more than 450 pounds and the linters, 250 pounds per ton of seed.

Cottonseed is purchased by oil mills on official grades in most areas of the Cotton Belt. However, this system of grading cottonseed is too elaborate, too expensive and time consuming to make its use practicable for application to individual lots as sold by farmers. For this reason, farmers usually sell to ginneries at average prices without regard to difference in quality of individual lots. This system of marketing involves an element of risk to ginneries as well as inequities to growers. Moreover, it does not provide an incentive to growers to produce high quality cottonseed.

### REQUISITES FOR A SMALL LOT GRADING SYSTEM

A method for grading small individual lots of cottonseed must necessarily be simple, rapid and inexpensive for use in settlements between ginneries and producers. Factors of quality of major importance are: oil content, moisture content, protein content, free fatty acids content of oil, linters content, and foreign matter content. The oil content is the most important single factor since it alone accounted for from 43 percent to 60 percent of the entire value of cottonseed during the past 30 years.



EVALUATION OF METHODS  
FOR MEASURING THE OIL CONTENT OF COTTONSEED

Official USDA Grading Method

The present official USDA method for analyzing cottonseed (including oil content) has been in use for the past 20 years. 1/ This method consists of pre-drying the cottonseed and thereafter fuming in a porous vessel containing hydrochloric acid. The fumed sample is ground, mixed and duplicate samples are accurately weighed and wrapped in filter papers for extraction. After a four hour extraction with petrolic ether (Skellysolve F or equivalent), the solvent is evaporated and the extracted oil weighed.

Although this method is quite satisfactory for use in the laboratory, the technical personnel and equipment required in such a process renders it beyond the scope of a small lot grading system. Moreover, the time required (24 hours) for completion of the analysis would make its use impractical for that application.

Direct Evaporation Method

A method of oil assay based upon the rapid evaporation of an extract, using carbontetrachloride as a solvent, was investigated. 2/ This process, a modification of the USDA official method, involved the maceration and extraction of cottonseed with carbontetrachloride in a blender for ten minutes. Prior to the extraction, the seed was first subjected to a one minute flaming for lint removal and then ground in a household food chopper. The extract was pressure filtered and five milliliter aliquots of the extract placed in tared aluminum foil evaporating dishes. The solvent was removed by heating on a hot-plate at 105°C for 15 minutes. The residual oil in the evaporating dish was weighed and the oil content of the cottonseed determined.

The results of this method compared favorably with that of the official USDA method (table 1). However, further study revealed two serious disadvantages in adapting this method for use in grading small lots of cottonseed. First, an extremely accurate analytical balance was needed for weighing the residual oil. It is questionable that it would withstand the vibration and dust conditions which may be prevalent

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1/ This method is similar to the American Oil Chemists' Society official and tentative methods of analyses (Aa 7-44) and to the National Cottonseed Products Association official methods of analysis.

2/ Investigation made by Battelle Memorial Institute, Columbus, Ohio, under contract with the U. S. Department of Agriculture.



around cotton gins. The operation of this instrument would also require considerable skill. Second, the 30 minute period required for the completion of an analysis would preclude the use of this method. For successful use in gin grading, an analysis must be completed in about 10 minutes.

Table 1.--Comparison of results obtained by official USDA and direct evaporation methods

Sample	Moisture	Analysis by Official	Analysis by Direct
		USDA Method	Evaporation Method
		Oil	Oil
		Dry	Dry
		Basis	Basis
	Percent	Percent	Percent
A.....	10.0	23.2	23.3
B.....	17.0	21.7	21.8
C.....	9.5	24.1	24.2

#### Specific Gravity Method

Measurement of the specific gravity of an extraction of cottonseed oil in a suitable solvent was investigated. A Faulk hydrometer was used in determination of the specific gravity. (6) <sup>3/</sup> This instrument is essentially a float with an attached chain of sufficient weight so that the float remains totally immersed in the test liquid. The chain and volume of the float determine the range of the hydrometer.

In spite of closely controlled temperatures, specific gravity determinations on oil-solvent mixtures did not give a reasonable correlation with the percent oil in the mixtures.

#### Salting-Out Method

The "salting-out" or precipitation of cottonseed oil from an oil-solvent extract is based upon the addition of a precipitant and the volumetric measurement of the precipitant-oil. Two general types of investigations were observed: (a) Use of a water soluble extractant and an aqueous precipitant; (b) use of a water soluble extractant and

<sup>3/</sup> Underscored numbers in parentheses refer to Literature Cited,  
Page 28.

a non-aqueous precipitant. In preliminary tests, isopropanol was used as an extractant since it was inexpensive, readily available and a reasonably good oil solvent. Several oil-isopropanol extractants were prepared to represent seed of varying oil contents. To the extraction, a water in ethyl alcohol mixture (50 percent alcohol by volume) was added and the mixture shaken. An aliquot of each was centrifuged, the tubes removed and the height of the interface was read. The results of this method were reasonably accurate.

A series of tests were then made extracting the oil from cottonseed. The cottonseed and solvent were placed in a high speed grinder (cutter blade revolving at about 15,000 r.p.m.). Upon inspection, a large number of whole seed and meats were found, resulting in poor extraction. It was concluded that the density of isopropanol was not sufficiently high for efficient maceration of the seed in the grinding operation. Therefore, water soluble oil solvents with specific gravity of 1.0 or more were believed necessary for proper preparation of the sample. These desired properties were found only in the chlorohydrins. However, because of the toxicity of these materials their use was considered too hazardous.

Investigations proved that the water soluble extractant and non-aqueous precipitant were much less promising than the other group. No precipitants were found which gave a complete separation of the oil. As a result, it was concluded that cottonseed oil is not sufficiently insoluble in any organic material (that is, precipitant), for this system to be successful.

#### Refractive Index Method

A successful method of measuring the oil content of cottonseed was developed and reported by Wesson (15). This method employed refractive index measurements of cottonseed oil - Halowax (monochloronaphthalene) extracts. This method was therefore given careful consideration.

It was believed that a suitable refractometer would be too expensive and would require considerable technical skill for operation. Also, the necessity of a high purity solvent made the use of this method questionable. This method was therefore considered unsuitable for a simple rapid oil determination at gins.

#### Infra-red Absorption Method

A preliminary evaluation indicated that there are several absorption maxima, any of which might presumably be used for the oil measure-

ment of cottonseed. <sup>4/</sup> However, since the required equipment would be rather expensive and complicated, further work on this method was discontinued.

#### Dielectric Constant Measurement Method

Any oil determination method successful in a small lot grading system must be rapid, requiring ten minutes or less for an analysis. The necessary equipment should also be rugged and easy to operate, with minimum testing techniques required as well as minimum handling of the sample.

An electrical measurement of the oil content of an oil-solvent mixture appeared to be a logical approach since the time required for a dielectric constant or conductivity measurement should be little more than one minute. The equipment for such determination normally can be designed for extremely stable and rugged use. When such instruments are made for use of one type mixture, they are easy to operate, requiring no special skill to obtain accurate results. For such measurement, it would be necessary to introduce an oil solvent mixture into a test cell, observe a meter reading, then empty the cell. Preparation of the oil-solvent mixture would be essentially the same as for any other proposed method.

#### THEORY OF DIELECTRIC CONSTANT MEASUREMENTS

The molecules of a material will, when the substance is placed in an electrical field, tend to orient themselves in a definite pattern with respect to the direction of the field. The dielectric constant of the material can, for simplicity, be defined as a measure of the degree to which the individual particles are oriented or the material polarized. For any substance, the dielectric constant is a definite and fundamental characteristic. Theories as developed by Debye, Falkenhagen, Smyth and others have been successfully applied to experimental results in this field.

Determinations of the dielectric constant, dielectric loss and conductivity have been used for a number of years with varying degrees of success for analyzing and studying the composition of gases, liquids and solids (2), (3), (5). The electrical measurement can be made in several ways. The choice of the method depends on the kind of sample, the accuracy desired in the determination and other factors such as cost and operational convenience of the equipment. In recent years, interest in high-frequency oscillation titrators has led to the develop-

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<sup>4/</sup> Investigation made by Battelle Memorial Institute, Columbus, Ohio, under contract with the U. S. Department of Agriculture.



ment of several instruments useful in measuring certain dielectric properties of liquid samples. (1), (4), (7), (14). Although in most of the investigations the instruments have been used to indicate the end-point of titrations, some progress has been made toward using the electrical oscillators (and associated detectors) for direct analysis of binary (and in one known instance, tertiary) mixtures (12), (13). The measurement of the dielectric properties of solids and of liquids has also been successful in continuous process applications (8), (10).

In using a dielectric measurement for routine analyses of a binary mixture, it is relatively unimportant whether the instrument indication is affected by only the dielectric constant or by both the dielectric constant and the dielectric loss of the samples tested. If the mixtures are stable, then with proper cell and circuit design, an empirical calibration with a high degree of accuracy can be developed. This technique has been used with several commercial electronic meters.

#### DEVELOPMENT OF AN OIL DETERMINATION METHOD BASED ON DIELECTRIC MEASUREMENT

##### Electronic Measurement of Dielectric Constant

The usual technique for measuring dielectric constants consists of determining the capacitance of a test cell with air as the dielectric  $C_a$ , and then with the sample as the dielectric,  $C_s$ . Then under ideal conditions, the dielectric constant,  $k$ , is:

$$k = \frac{C_s}{C_a}$$

Since it is impractical to design a cell with no residual capacitance, the equation must be modified slightly. The exact form of the equation then depends on whether the residual capacitance is in series or parallel with the variable capacitance of the cell. In either case, the variable (or effective) capacitance of the cell can be readily determined by the use of samples of known dielectric constant. The National Bureau of Standards has published a listing of liquids suitable for use as standards (9). Of these, Benzene and Chlorobenzene were found to be available in high purity and to be very useful in determining the effective capacitance of test cells.

The choice of an instrument for dielectric measurements, as suggested previously, depends on the kind of sample, the accuracy required in the determination and the final purpose of the analysis. In the preliminary investigations of this study, an impedance bridge and null detector were used to obtain information on the various possible solvents and the variability to be expected between lots of cottonseed oil. For this purpose, a bridge was considered most appropriate since both the



dielectric loss and dielectric constant could be measured. This equipment was also used in the first tests with oil-solvent mixtures and served occasionally throughout the studies as a method of measurement.

After it was established that the dielectric measurement could be used for the determination of the oil content in oil-solvent mixtures, the following requisites for an acceptable instrument were determined:

1. The electronic circuit and test cell must be rugged and stable.
2. The meter should be direct reading or require only one adjustment for each determination.
3. The equipment should be designed for commercial production and minimum cost.
4. Temperature compensations, control or measurement should be made as simple as possible without excessive cost.

Guided by these criteria, the circuit shown in figure 1 was developed. <sup>5/</sup> This meter was constructed and has been successfully used for several years with only slight modifications.

#### SELECTION OF THE SOLVENT

In the selection of a solvent, the following requisites were considered:

1. The solvent should be an excellent oil solvent and be neither soluble in water nor a solvent for water.
2. The dielectric constant of the solvent should differ as much as possible from that of cottonseed oil (which is approximately 3) and the dielectric loss should be small.
3. The boiling point should be high enough to minimize evaporation loss during grinding, extraction and filtering.
4. The specific gravity (1.2 or greater) should be such as to provide efficient maceration of the cottonseed during grinding-extraction.
5. The solvent must be readily obtainable, not excessive in cost, and of uniform high purity (especially as regards dielectric value).
6. The solvent must not be too toxic or inflammable.

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<sup>5/</sup> Leader in this work was Harry F. Cooke, now located at American Radio and Television Corp., Little Rock, Arkansas

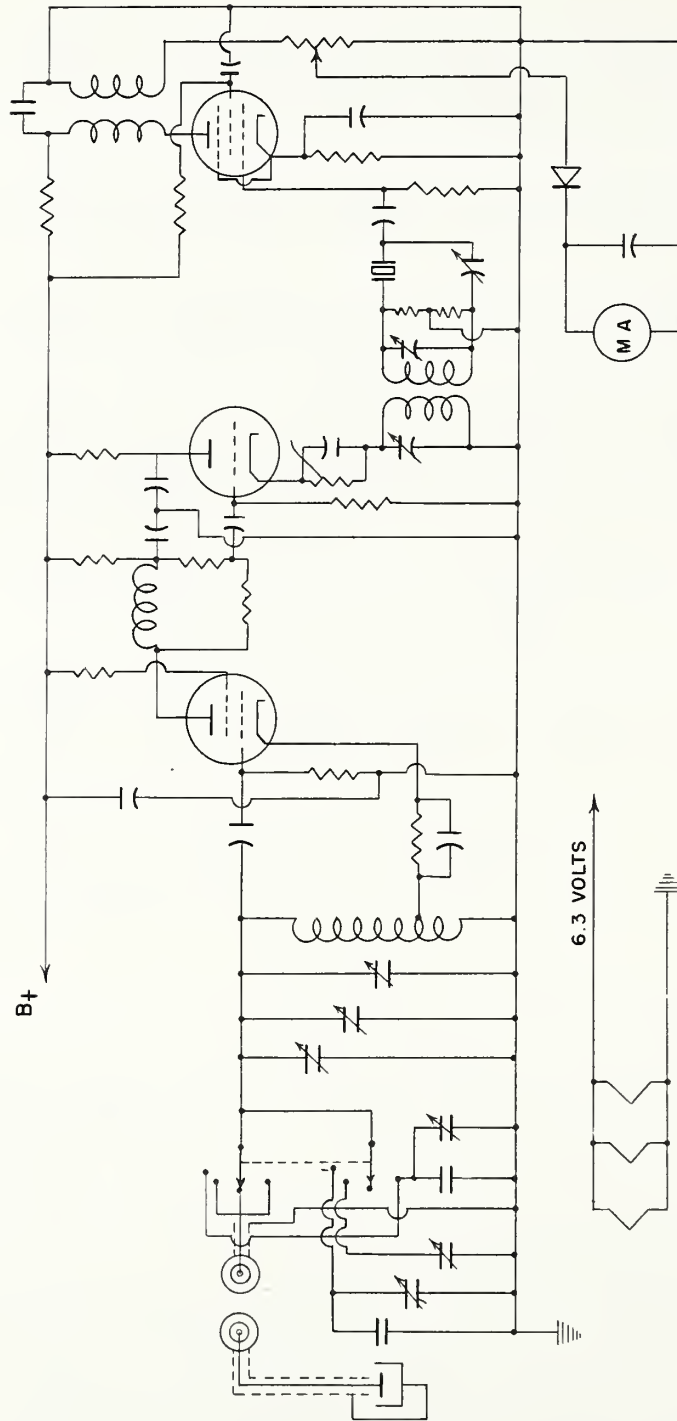


Figure 1.--Electrical circuit for the USDA Cottonseed Oil Meter

After an investigation of more than 100 possible solvents, it was apparent the chlorinated aliphatic and aromatic hydrocarbons offered more promise than any other types of compounds. Of these, trichloroethane and orthodichlorobenzene appeared to best satisfy the necessary qualifications.

According to the data furnished by manufacturers, trichloroethane has a dielectric constant of 8.6, is stable and is insoluble in water. It is also economically available and of low toxicity. On the other hand, the vapor pressure is relatively high and there was considerable question as to the availability of this solvent at a uniform purity.

Information on orthodichlorobenzene indicated that this material has all the desirable properties of trichloroethane and, in addition, a much lower vapor pressure. Also, this material was commercially available with less than one percent impurities and at relatively low cost. In view of these desirable properties, orthodichlorobenzene was chosen as the solvent.

#### METHOD OF SAMPLE PREPARATION

Early in the investigations, it became evident that the rapid extraction of the oil from the cottonseed would be a necessary part of any test procedure. Several possible ways of removing the oil from cottonseed with a solvent were investigated and at least two were successful. One method consisted essentially of a coarse grinding of the cottonseed to break the hulls and meats, followed by an extraction in which the solvent and ground seed were agitated in a high-speed mixer. Although this process gave acceptable results, the excessive handling of the samples was a definite disadvantage.

While this work was in progress, a manufacturer of laboratory equipment introduced a high speed grinder that proved satisfactory for extracting oil from cottonseed. (fig. 2) It is an impact cutter type grinder-extractor consisting of a rapidly rotating shaft with a shaped sharp blade at its extremity. The spindle speed is 15,000 r.p.m. and the blade tip speed is 135,000 inches per minute. It is powered through a "V" belt by a 3/4 h.p. motor. The temperature of the seed-solvent mixture is maintained at about 35°C., by a water cooled cup during the five minute grinding operation. Various speeds and time intervals were tested in order to determine the optimum operating conditions. Using 50 grams of cottonseed in 275 grams of solvent, a complete extraction was obtained in five minutes. Increasing the time interval had no measurable effect on the completeness of the extraction. Incomplete extraction resulted from slower grinding speeds and smaller ratios of solvent.

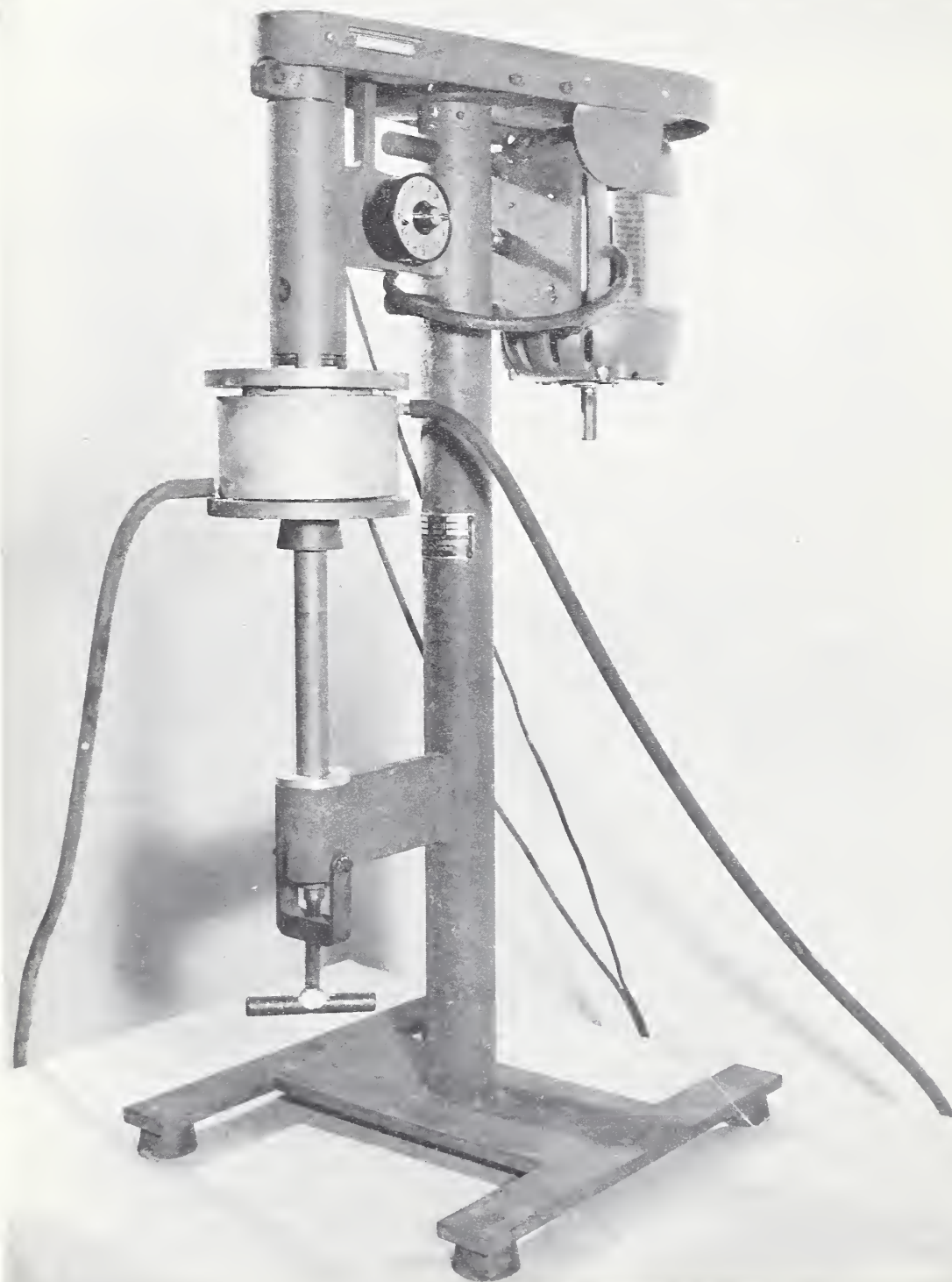


Figure 2.--Grinder-extractor used for preparation of cottonseed oil-orthodichlorobenzene solutions upon which dielectric determinations are made.



Although water is considered to be insoluble in orthodichlorobenzene, small amounts were picked up by the extract during the grinding process. Because of the high dielectric constant (81) and dielectric loss of water, minute amounts contained in the extract produced substantial changes in the dielectric properties of the mixture. To circumvent this difficulty, a quantity of a desiccant was added to remove the water from the extract. Anhydrous calcium chloride (20 mesh or finer) was found to be an effective drying agent providing the extract temperature did not exceed 40°C (fig. 3). Activated alumina was found to be unsatisfactory due to inadequate drying of the extract when using an eight mesh or larger size granule, and because it indicated a tendency to adsorb oil. Anhydrous powdered aluminum oxide was a satisfactory drying agent; however, it caused excessive dulling of the cutter blade. The use of silica-gel was prohibitive due to the high price of this product. It also indicated a tendency to adsorb oil. Other desiccants tried either reacted with the oil or otherwise affected the results.

The desiccant not only removed the water from the extract but also removed the moisture in the seed during the grinding operation. This dry condition of the ground seed-solvent mixture materially increased the speed of filtration, particularly when seed of high moisture content were being assayed. (Considerable difficulty was experienced in filtering all non-dried oilseed extracts when the moisture content of the seed was high).

#### FILTRATION OF EXTRACT

Effective filtration may be accomplished by either vacuum, pressure or centrifugation. Of these three methods, the first two appeared to offer the most economical and practical approach to this particular problem. Vacuum filtration requires a dependable source of vacuum and could be most easily carried out by using a water aspirator as the vacuum source, filtering with a Buchner funnel. Commercial filter paper would serve as the filtering medium. A disadvantage of vacuum filtration, however, was found to be the loss of solvent by evaporation while the extract was under reduced pressure. The additional handling of the extract was also a disadvantage as it increased the probability of contamination.

The two types of pressure filters considered were mechanical press and air pressure filters. Both were used. First, the ground seed-solvent mixture was pressed in an ordinary household ricer to remove most of the linters, hulls and other larger solids. An air pressure filter was then used to remove the fines. The air pressure filter designed and fabricated for this purpose is made in two parts (fig. 4). The lower part is the filtering base and is mounted directly over the test cell. The upper section of the filter or the air chamber

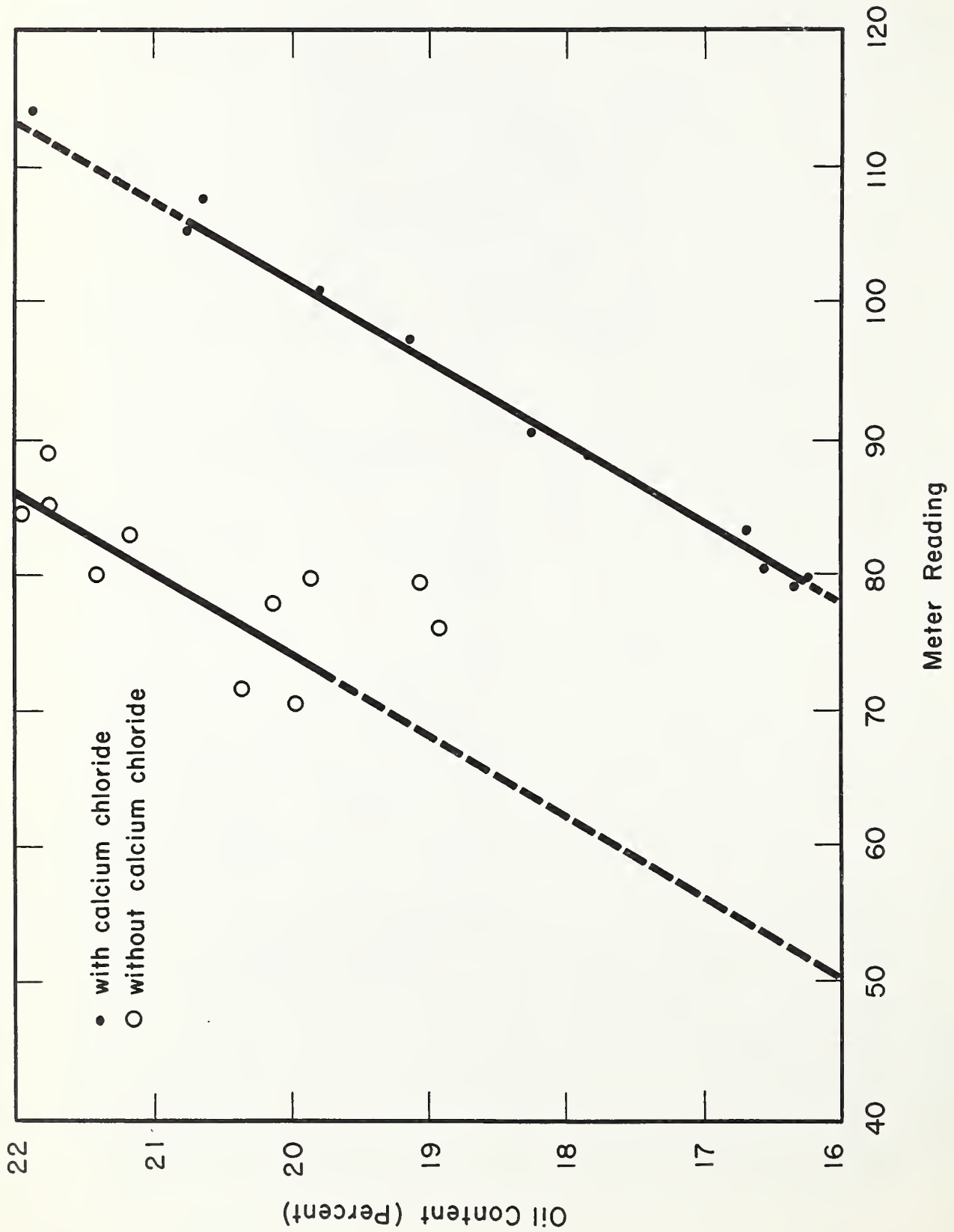


Figure 3.--Comparison of results obtained with and without the use of anhydrous calcium chloride as a drying agent during grinding-extraction.

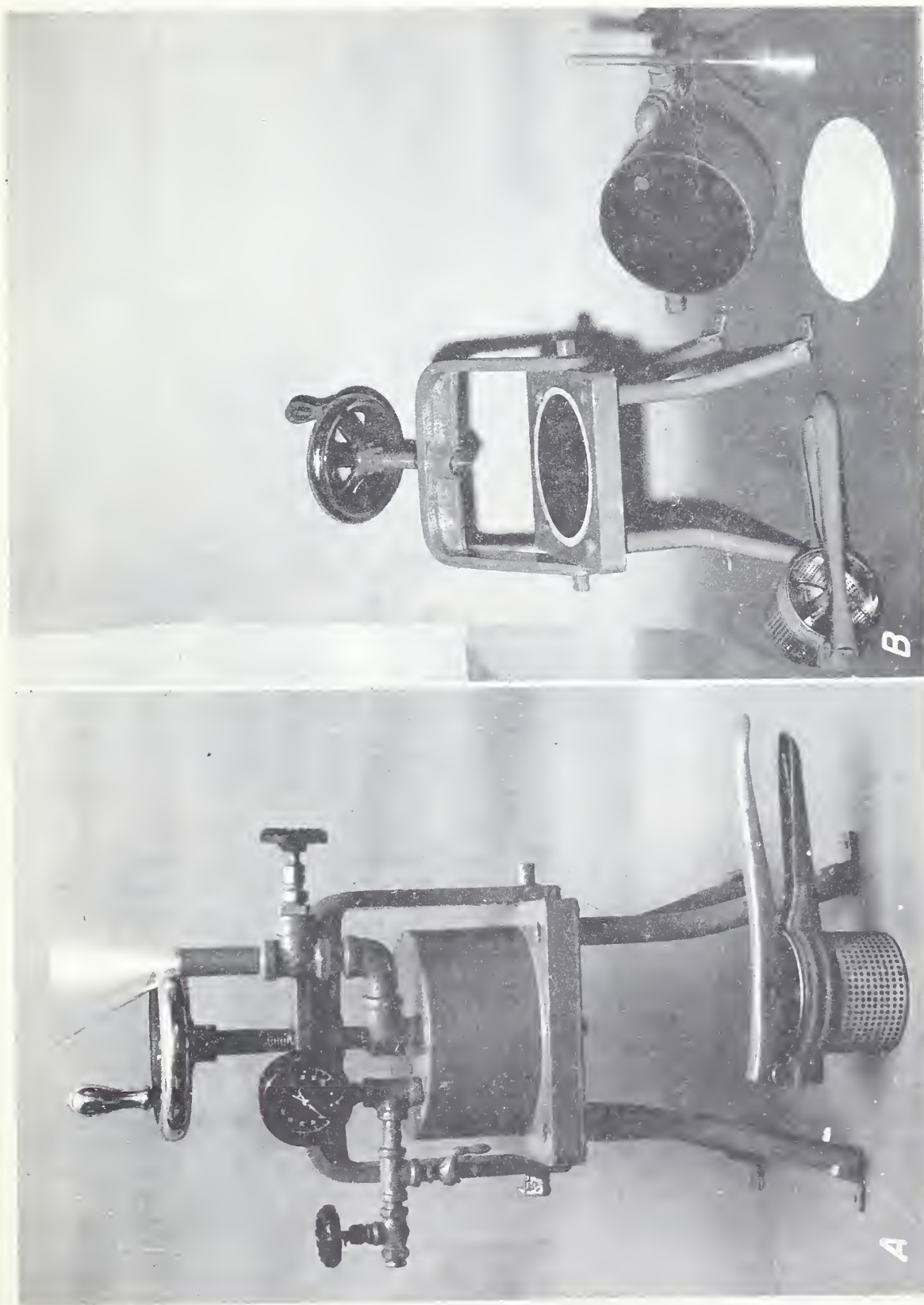


Figure 4.--Mechanical and air pressure filter used in removing solids from the oil-solvent mixture. (A - assembled) (B - dismantled).



is removable and contains the inlets for the air pressure, the extract, and the gauge for air pressure readings. In operation, a piece of strong retentive filter paper is placed over the circular grooved filtering area in the base. The air chamber cylinder is then placed directly over the filter paper so it is centered on the teflon seal located around the outside of the filtering plate. The overhead clamp is positioned directly over the center of the top and the clamp screw is tightened until a seal between the air chamber and the filtering base is made. In operation, the extract inlet is opened and the extract is poured into the ricer held in position over the inlet funnel. Pressure is applied with the metal plunger forcing the extract through the perforated sides and bottom. The larger particles remain in the hand press. After the introduction of the extract, the inlet valve is closed and pressure of about five pounds per square inch is applied. After filtration is complete, the air valve is closed, the clamp is loosened and the air chamber is removed. The filter paper containing the residue is removed and discarded. The filtering base and air chamber are then wiped clean and the operation is repeated for another sample.

#### TEST CELL DESIGN

In the development of a test cell, the following basic requirements were considered: (1) The cell must be rugged to prevent capacitance changes due to rough treatment; (2) the cell, when filled, must not retain air bubbles in the electrical field and when drained, essentially all of the sample must be evacuated; (3) the capacitance of the cell must be adjustable within a narrow range in order to provide for variations in dielectric constant corrections between shipments of solvents.

During the development of the cell, several different designs were considered. Some models were constructed to allow disassembly for cleaning. Parallel plates as well as concentric cylinders were used as condensers.

The cell used in this work consists of two concentric metal cylinders (fig. 5). The inner cylinder (with both ends sealed) is suspended in and electrically insulated from the outer cylinder. The space between the two cylinders, forming the condenser, is maintained by a rugged mounting system. Conical depressions in the top and bottom serve as the only supporting points for the inner cylinder. The supporting rods may be adjusted thereby changing the position of the inner cylinder with respect to the outer cylinder, allowing the electrical capacitance of the cell to be set at a desired value. The outer cylinder is at ground potential; therefore, no special electric shielding is needed. Since all surfaces within the cell are at least 45 degrees from the horizontal, no difficulty with air drainage or bubbles has been encountered. Temperature sensing elements were mounted in the end caps



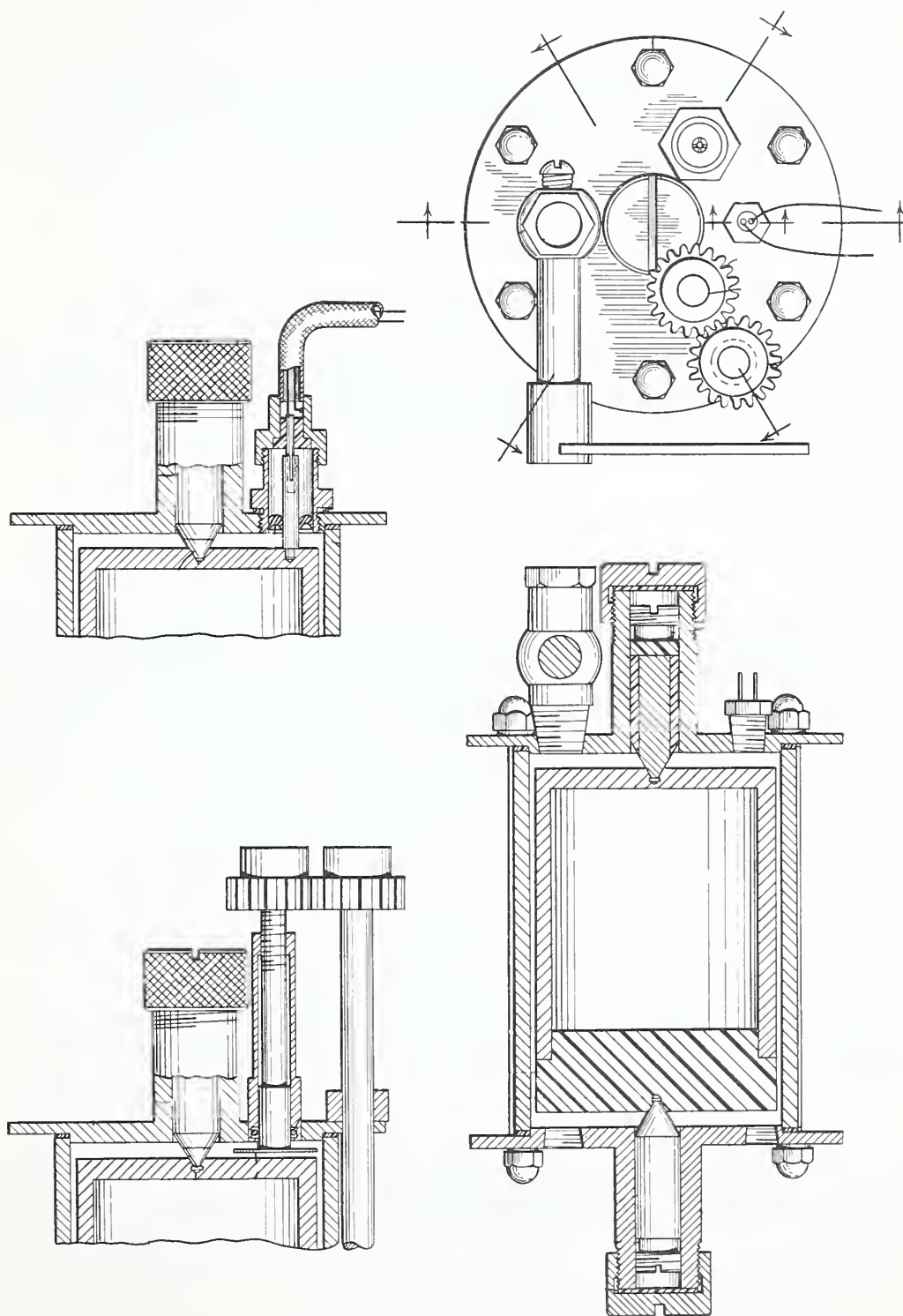


Figure 5.--Detail views of the oil meter test cell.

and are, when the cell is filled, immersed in the test liquids. (These elements are not used, however, since the cell temperature is controlled).

A small plate mounted in one end-cap acts as a trimmer condenser. The capacitance of the cell is changed when its distance to the inner cylinder is varied. This trimmer is used to adjust the meter reading to a pre-determined value with solvent in the cell. In this manner, the small variations between batches of solvent is compensated for.

The total cell capacitance,  $C$ , (neglecting fringe effects) is:

$$C = C_v + C_p$$

where  $C_p$  is the fixed capacitance, and  $C_v$  is the variable capacitance of the cell. By using air as the reference point for all measurements, the change in capacitance caused by a sample is:

$$M = KC_v + C_p - C_v - C_p$$

$$M = KC_v - C_v$$

Since  $M$  is the meter indication (or dial divisions) it is easily seen that the meter could be directly calibrated in dielectric constant.

$C_v$  consists of two capacitances, the main part of the cell  $C_c$  and the trimmer condenser  $C_t$ . Then,

$$C = C_c + C_t + C_p$$

The measurements all being made as differences in capacitance,  $C_p$  can be omitted.

$$'M' = K(C_c + C_t) - (C_c + C_t)$$

For a material of different dielectric constant,  $K'$ , the trimmer condenser,  $C_t$ , can be adjusted to give the same meter indication, ' $M$ '. In which case,

$$K(C_c + C_t) - (C_c + C_t) = K'(C_c + C_t') - (C_c + C_t')$$

$$C_t' = \frac{C_c(K' - K) + C_t(K - 1)}{(K' - 1)}$$

This technique corrects for the major part of the error introduced by slight variations in the dielectric constant of the solvent. It can also be shown that the curves of dielectric constant of extract versus the percent contained oil will have slightly different slopes for solvents of different dielectric constants; therefore, even with the trimmer condenser, it is necessary to have a solvent supply that does not differ appreciably between lots.

#### EFFECT OF TEMPERATURE

One of the disadvantages of orthodichlorobenzene as the solvent in this process is the rather large effect of temperature on its dielectric constant. In the "Table of Dielectric Constants of Pure Liquids" (9), orthodichlorobenzene is listed as having a dielectric constant of 9.93 at 25°C., with a temperature coefficient (a) of .00194. The following equation is given:

$$\text{Log } k_2 = \text{Log } k_1 - a(t_2 - t_1)$$

where "k" is the dielectric constant, "t" is in degrees centigrade, and the logarithms are to the base ten.

As an approximation of the effect of temperature on an oil-solvent mixture, the oil can be neglected. The curve in figure 6 represents the change in dielectric constant of the solvent with changes in temperature. For acceptable accuracy in the oil determination, the dielectric constant must be measured to  $\pm 0.003$ . Since the effect of temperature on the dielectric is approximately 0.04 per degree centigrade, it is obvious that the temperature must be controlled (or measured) within  $\pm 0.05$  degree centigrade.

Two methods of compensating for temperature were tried. One system employed temperature control of the cell in an oil bath at 50 degrees  $\pm 1^\circ$  centigrade and temperature measurement of the extract in the test cell to an accuracy of  $\pm 0.01$  degree centigrade. Thermistors were used as sensing elements for the temperature measurement. For short periods of time, this process was satisfactory; however, the thermistor drift necessitated frequent checking at a reference temperature with a standard thermometer.

Later, a constant temperature bath was used, the temperature controlled to less than  $\pm .05^\circ\text{C}$ . This control in conjunction with a heat exchange tube, through which the extract flows to the cell, proved to be completely satisfactory.

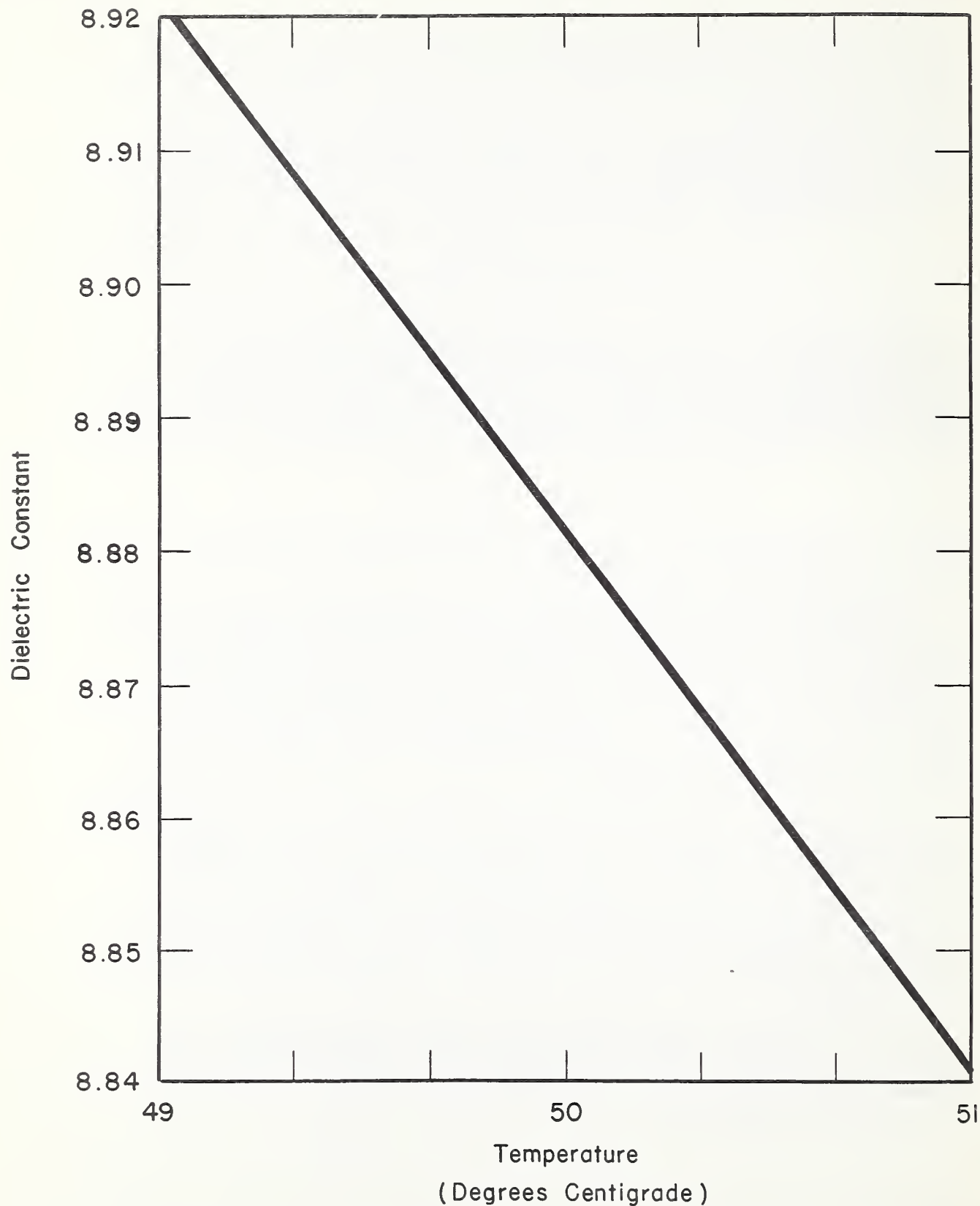


Figure 6,--The effect of temperature upon the dielectric constant of orthodichlorobenzene - pure.



## DESCRIPTION OF TESTING EQUIPMENT

### Electronic Meter

The oil meter is essentially a substitution type radio frequency capacity meter and a cell suitable for measuring liquid dielectrics. The instrument is adjusted to resonance (indicated by a meter) with a fixed condenser in the circuit; the test cell filled with the liquid to be measured is substituted in the circuit for the fixed condenser and a calibrated variable condenser is used to retune the instrument to resonance.

A block diagram of the instrument and a simplified circuit of the radio frequency oscillator is shown in figure 7. Included in the tank circuit of this oscillator is the calibrated variable condenser,  $C_6$ , and the zeroing condensers,  $C_7$  and  $C_8$ . By switch  $S_1$ , several pre-set condensers, and the test cell become part of the tank circuit in various combinations. The tank circuit is initially adjusted so that the frequency of the oscillator will be 455 kilocycles when switch  $S_1$  is in first position and with condenser  $C_6$  set to an arbitrary value. 6/

The output of the oscillator is fed into a cathode-follower amplifier, and then into a crystal filter tuned to 455 kilocycles. The signal is then amplified and rectified. The magnitude of the signal is then indicated on a one milliamper meter. When the oscillator is tuned to 455 kilocycles, the radio frequency voltage passes through the crystal filter and causes a large deflection of the meter. If the oscillator is tuned slightly above or below 455 kilocycles, the crystal filter does not pass the signal and the meter deflection is small.

With the test cell filled with a sample and substituted in the tank circuit for the fixed condenser, condenser  $C_6$  is adjusted to give maximum deflection of the meter, indicating that the oscillator is tuned to 455 kilocycles (the reference point). Condenser  $C_6$ , (and dial) can be calibrated in capacitance of the test cell, dielectric constant of the liquid sample, percent oil content of the sample 7/ or any similar terms.

### Pressure Filtration

The rapid filtration of the extract as described on page 11 is accomplished in two to three minutes. Most of the large particles are retained by the hand press, the remainder by the air-pressure filter.

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6/ This value, for convenience of operation, should be approximately the mean capacitance of  $C_6$ ; and once the instrument is adjusted, the value is no longer arbitrary. Subsequent zero adjustments of the instrument must be done with  $C_6$  in this position.

7/ It is understood, of course, that if the dial is calibrated in percent oil content of the sample, the calibration is empirical and the procedure for obtaining samples must be the same for all samples.

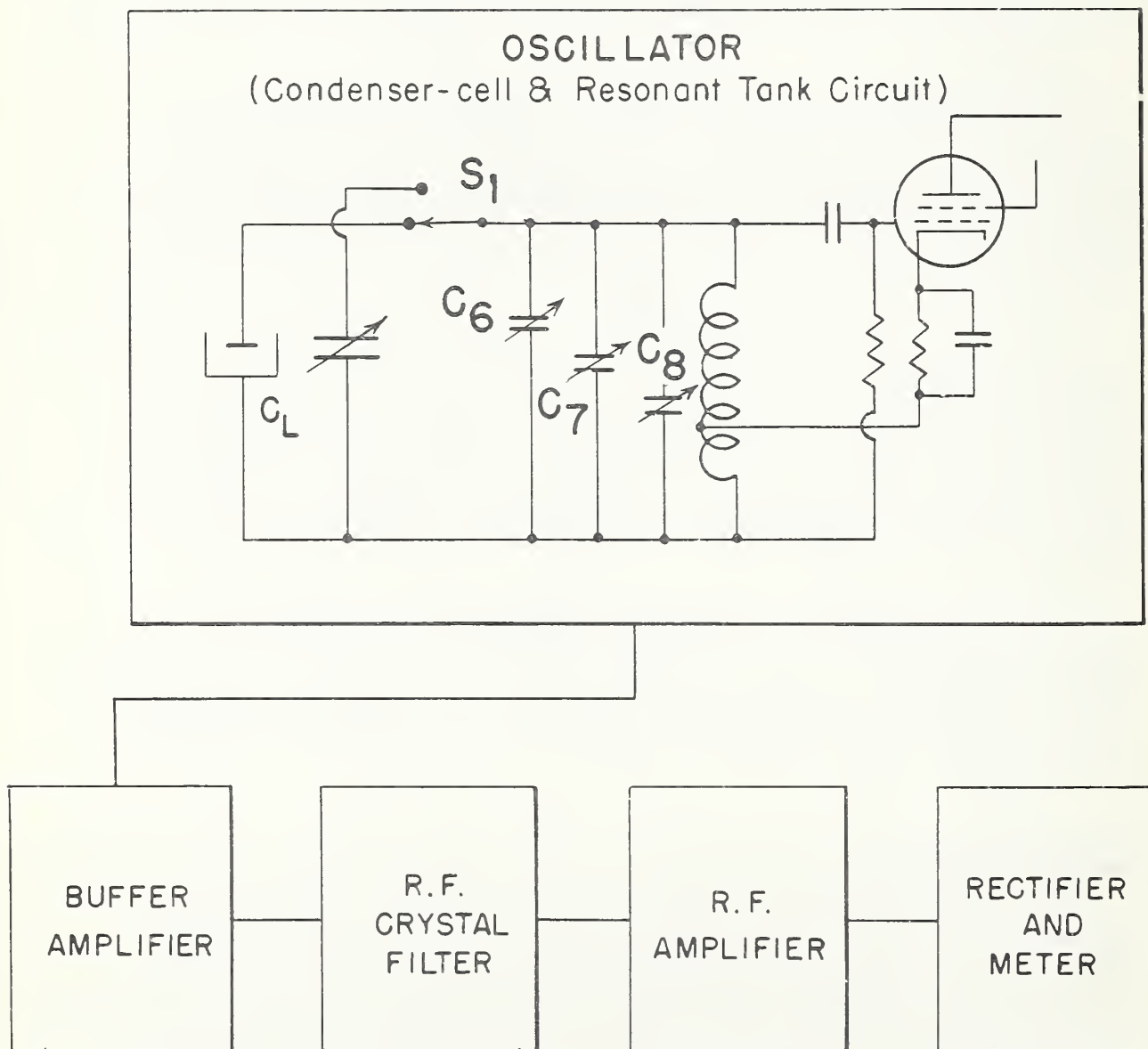


Figure 7.--Block diagram with simplified circuit of the radio frequency oscillator of the cottonseed oil meter.

## Test Cell

From the air pressure filter, the extract drains into the heat exchange tube (fig. 8). This tube is immersed in the temperature controlled oil bath and serves to bring the extract to the desired temperature while conducting it from the filter to the cell.

As described on page 14, the test cell is basically two concentric cylinders. The small trimmer condenser on the cell is adjusted through a combination of rods and gears.

## Temperature Bath

The test cell and heat exchange tube are fastened in a temperature controlled bath which is simply two metal boxes with an insulating material between them. (fig. 8) A heater, thermostat, and stirrer are provided to maintain the desired temperature throughout the bath. The bath also serves to support the pressure filter as well as the test cell.

## The Grinder

A modified high-speed commercially available grinder is used in most of this work; however, several modifications made it more adaptable to the process (see page 9). The equipment as supplied was rated at 15,000 r.p.m. and was powered by a 1/2 horsepower motor. It was found that a 3/4 horsepower motor was needed to obtain the necessary rated speed of 15,000 r.p.m. The aluminum cup was also equipped with a water-jacket to provide a means for cooling the extract.

## Testing

In evaluating the dielectric assay method for oil determination, a series of 120 samples of cottonseed were analyzed for oil and moisture contents by the official method of the U. S. Department of Agriculture. These samples were also tested for oil content with the dielectric method. The test cell temperature was not controlled but temperature measurements taken. An analysis of the results indicated a correlation of  $\pm .986$  between the two methods and a standard error of difference of  $\pm .229$ . (fig.9) The samples included cottonseed of several different varieties with oil contents varying from 15.5 percent to 21.8 percent and moisture contents from 7.0 percent to 21.9 percent.

A further series of tests were made using standard check cottonseed samples. During these tests, the cell temperature was controlled by the constant temperature bath. A General Radio Precision Condenser was substituted for the variable condenser in the meter in order to obtain greater range of measurement as several tests were made on different

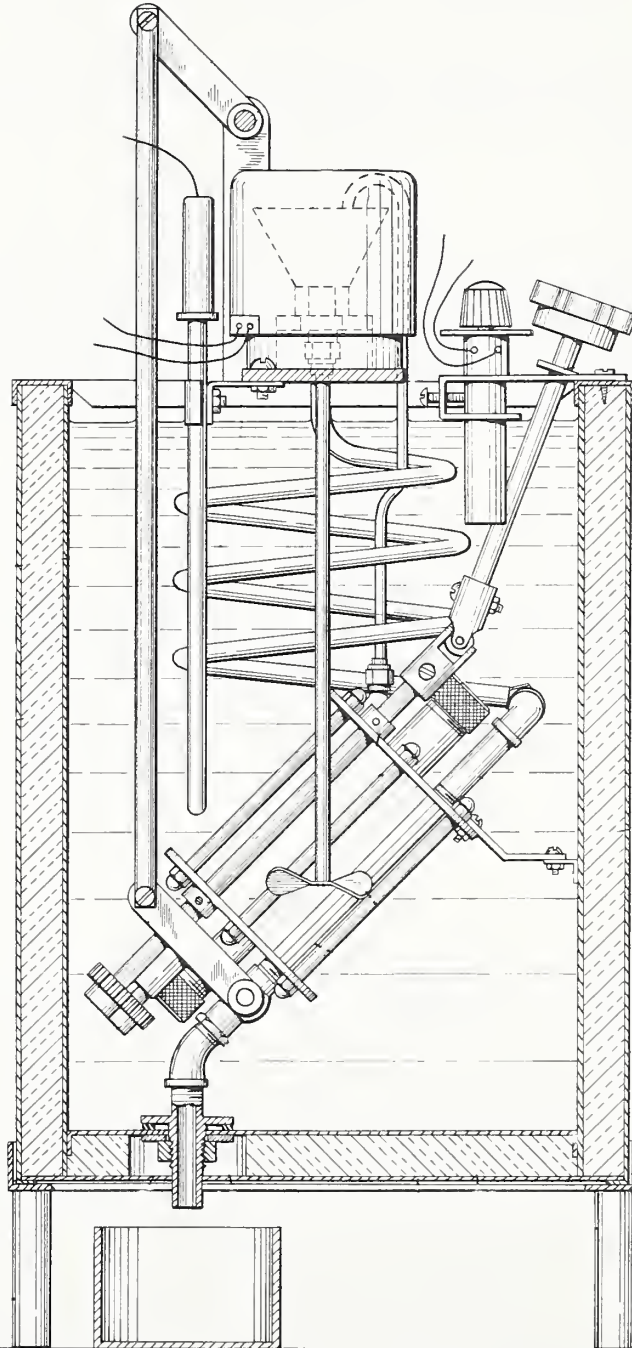


Figure 8.--Constant temperature bath cross-section showing test cell assembly, heat exchange tube and stirring mechanism.



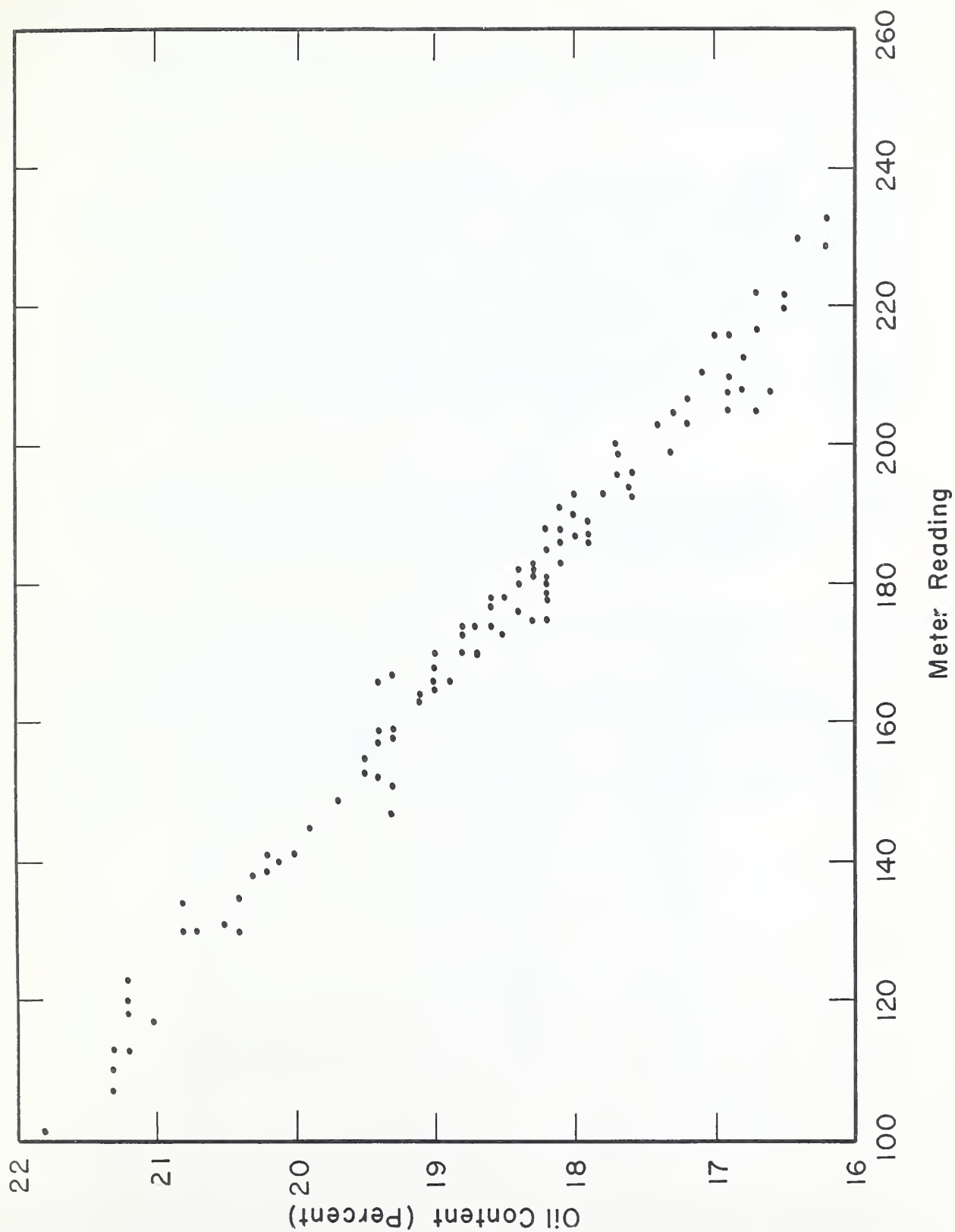


Figure 9.--Scatter diagram of oil content of cottonseed by USDA chemical method and by the dielectric oil meter.

lots of orthodichlorobenzene. An analysis of the results indicated a correlation of  $\pm 0.994$  and a standard error of difference of  $\pm 0.15$  percent oil. From these data, a calibration chart for the meter was made. (fig. 10)

To test the precision of the trimmer capacitance on the cell, a series of samples were extracted using solvents with slightly different dielectric constants. A difference of approximately 50 m.m.f. was found between the two solvents. Extractions were first made using the solvent with the higher dielectric constant. The cell was then filled with the solvent having the lower dielectric constant and the trimmer capacitance adjusted to give a meter reading corresponding to the solvent of higher dielectric. Extractions were made on the samples using the lower solvent. The results of these tests indicate that different lots of solvents which vary no more than 50 m.m.f. will give comparable results after the test cell is adjusted (table 2).

Table 2.--Comparison of meter readings and oil content of samples of cottonseed with solvent "A" and solvent lot "B" after the meter test cell was corrected for solvent "B"

Lot 1			:	Lot 2 Solvent		
Solvent			:	Scale Reading 494.6		
Meter Reading 544.3			:	Cell Adjusted to Read 544.3		
Sample	:	Meter	:	Sample	:	Meter
Number	:	Reading	:	Number	:	Reading
	:		:		:	
	:	m.m.f.	:		:	m.m.f.
	:		:		:	
	:	Percent	:		:	Percent
1.....	:	539.0	:	1.....	:	539.1
	:		:		:	
2.....	:	536.7	:	2.....	:	536.8
	:		:		:	
3.....	:	546.9	:	3.....	:	546.6
	:		:		:	
4.....	:	543.1	:	4.....	:	543.2
	:		:		:	
5.....	:	540.3	:	5.....	:	540.1
	:		:		:	
	:		:		:	
	:		:		:	

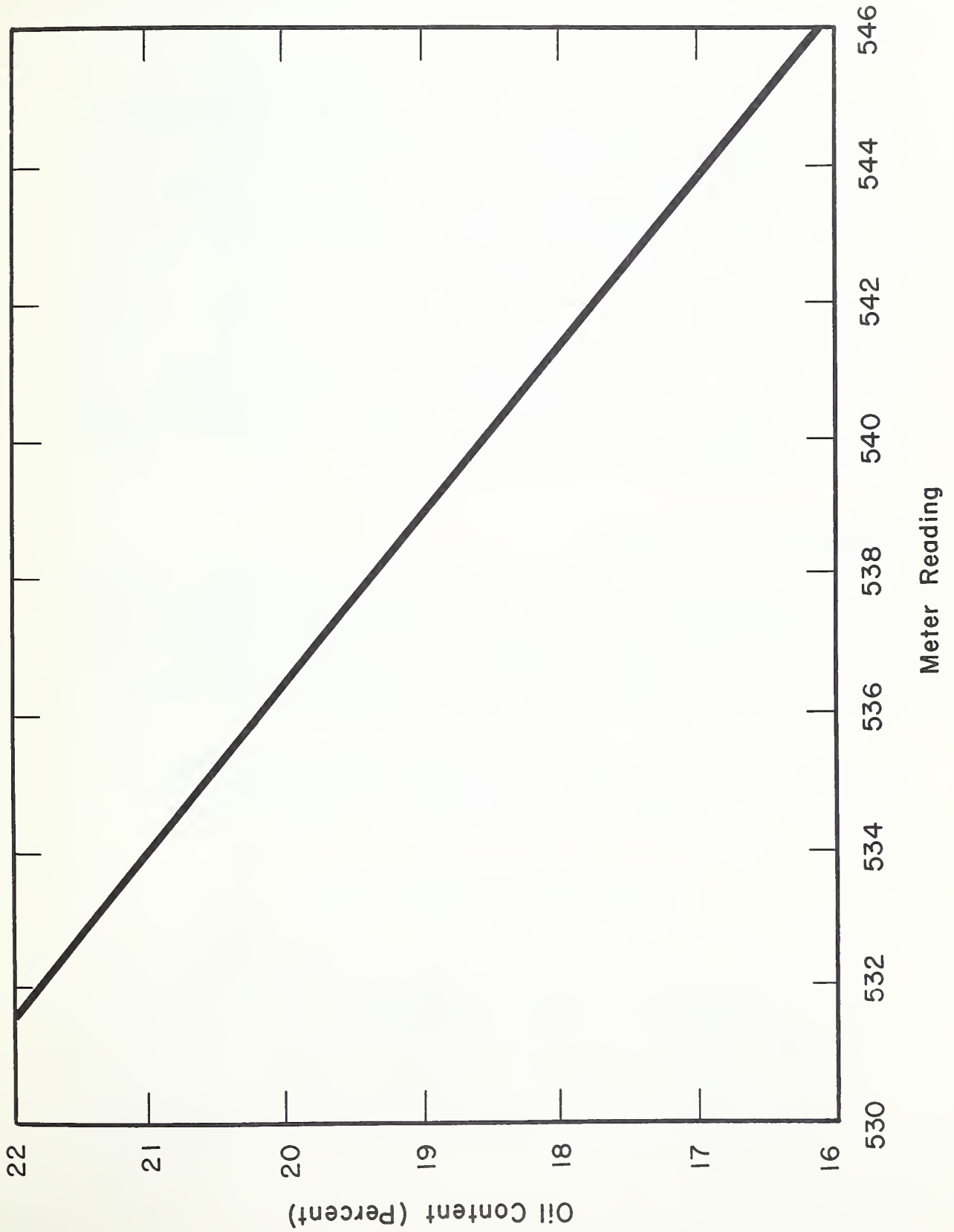


Figure 10.--Calibration chart for converting meter readings to oil content of cottonseed.

## TIME AND COST COMPARISONS

### Electronic Method of Analysis

A determination of the oil content of cottonseed may be completed in ten minutes by the electronic method. Preparation and grinding of the sample can be accomplished in seven minutes with the remainder of the time required for filtration of the sample and reading of the meter. While the first sample is being filtered, a second sample can be prepared and the grinding-extraction started. Since the grinding-extraction phase requires seven minutes while filtration and meter reading requires only three minutes, two grinder-extractors could be used for each meter-filter unit if the volume warranted. Under such circumstances, one hundred cottonseed samples could be processed in a little less than six hours by two operators which are required for the most efficient operation of this method. One person can operate two grinder-extraction units while the other handles the filtration and makes the meter readings. For 100 oil determinations, a total of about 12 man hours are required or 0.12 man hour per sample. In addition to labor cost, the expense for the solvent, filter paper, desiccant and electric power is estimated at \$0.16 per sample.

### Chemical Method of Analysis

The present official method of analysis for cottonseed (including the oil determination) requires 24 hours for completion of the test. However, during this time, any number of tests may be completed, depending upon the equipment and personnel. In completing 100 oil content determinations, about 13 man hours are required, or 0.13 man hour per sample. Supplies will cost an estimated \$0.09 per sample.

The above analysis does not take into account the initial and maintenance costs for equipment necessary for the chemical method of analysis. This equipment is considerably more expensive than that required for the dielectric determination.

## CONCLUSIONS AND RECOMMENDATIONS

Based on the foregoing results, it is concluded that:

- (1) The principle of dielectric measurement of the oil content of cottonseed is sound and practical.
- (2) The method is satisfactory from the standpoint of accuracy.
- (3) The method is sufficiently rapid to make its use practical for measuring the oil content of small lots of cottonseed at gins.



- (4) The facility with which oil content determinations can be made by means of the dielectric method and the accuracy of the results justify its consideration as an alternate method of oil assay in connection with the official method of grading cottonseed.

It is recommended that:

- (1) The dielectric meter and cell be redesigned for commercial manufacture.
- (2) Redesigned units be thoroughly field tested.

Literature Cited

- (1) Alexander, F. C., Jr., Dielectric Constant Meter. Electronics No. 18 (1945), p. 116.
- (2) Anderson, K. and Revinson, D., Use of High Frequency Titrimeter-Volumetric Determination of Beryllium. Analytical Chemistry, No. 22 (1950), p. 1272.
- (3) Blaedel, W. J. and Malmstadt, H. V., Volumetric Determination of Thorium by High Frequency Titrimetry. Analytical Chemistry No. 23 (1951), p. 471.
- (4) Blaedel, W. J. and Malmstadt, H. V., Direct Reading and Differential Frequency Meter for High Frequency Titrations. Analytical Chemistry No. 24 (1952), p. 450.
- (5) Blake, G. G., A New Method for Rapid Comparison and Measurement of Solution Concentrations Which Also Provides for the Automatic Control of Solution Strength, Chemistry and Industry, No. 3 (1946), p. 28.
- (6) Faulk, C. W., A New Form of Precision Hydrometer, Optical Society of America, No. 7 (1923), p. 327.
- (7) Fischer, R. B., Simplified Instrument for Wide Range Dielectric Constant Measurement. Analytical Chemistry, No. 19 (1947), p. 835.
- (8) Howe, W. H., Application of Dielectric Measurement to Continuous Processes. Instruments, No. 24 (1951), p. 1434.
- (9) National Bureau of Standards, Table of Dielectric Constants of Pure Liquids, Circular 514. National Bureau of Standards.
- (10) Thomas B. W., Faegin, F. J. and Wilson, G. W., Dielectric Constant Measurement for Continuous Determination of Toluene. Analytical Chemistry, No. 23 (1951), p. 23.
- (11) Wesson, David, New Optical Method for Determining Oil in Oil Mill Materials, Cotton Oil Press, March (1920), p. 70; April (1920), p.56.
- (12) West, P. W., Robichaux, T. and Burkhalter, T. S., Analysis of System Water-benzene, Methyl-ethyl-ketone. Analytical Chemistry, No. 23, (1951), p. 1625.
- (13) West, P. W., Semise, P., and Burkhalter, T. S., Determination of Water in Alcohols. Analytical Chemistry, No. 24 (1952), p. 1250.
- (14) West, P. W., Burkhalter, T. S., and Broussard, L., High Frequency Oscillator Utilizing Heterodyne Principle to Measure Frequency Changes Induced by Diverse Chemical Systems. Analytical Chemistry, No. 22 (1950), p. 469.



